Efficient recovery of aluminum from saline slag wastes

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Abstract

This work presents the procedure to improve the aluminum extracted from a hazardous waste from the recycling of aluminum, aluminum that could be used in the production of value-added materials, as well as with the generation of non-hazardous waste. The aluminum waste was treated under reflux and stirring with NaOH aqueous solutions taking into account two concentrations (1 and 2 mol/dm^3), various times of extraction (1, 2 and 4 h) and 4th consecutive steps of extraction in order to obtain solutions with Al^{3+}. The activation of the waste by milling is also analyzed. After extraction, the solution is filtered to separate an aqueous solution that contain the extracted Al^{3+} and a residual waste. A maximum of 7.54 g/dm^3 of aluminum was extracted in the first step, for a total accumulated of 9,59 g/dm^3 of aluminum. The extracted aluminum can be used to synthesize added-value products applied as adsorbents and catalysts. Finally, the residual waste generated was characterized by N_2 adsorption at -196 °C, X-ray diffraction, X-ray fluorescence, energy-dispersive X-ray and scanning electron microscopy in order to apply it as in future works adsorbent or catalyst.

Keywords: industrial waste valorization, high-value-added products, aluminum extraction, alkaline extraction, hazardous waste.

1. Introduction

The main problems associated with the aluminum saline slags management are the large area of land required for disposal, toxicity associated leached to atmosphere and to groundwater and the high cost involved in road transportation. The costs are function of the type of waste, distance from the industry to the landfill, transport, weather, regulations and potential uses [1]. When the dump is close to the industry and the aluminum waste is easily manipulated management costs are low, from €3.00 to €5.00. The costs increase up to €40.00 if the distance is long, waste manipulation is complicated or a new deposit place is needed, because Al waste management does not end when it is placed in a landfill, future space is mandatory too. The use of Al, especially recycled Al, increases every year and generates millions of tons of wastes. The 95% of aluminum saline slags are landfilled, with a cost of M€80 [2].

Disposal is not required if aluminum saline slags are valorized and present and future landfills are not needed. So, recycling aluminum saline slags instead of disposal is the best solution to solves environmental concerns and also creates new economic opportunities. Potential applications for aluminum saline slags as a raw material are being studied in the last years in construction, polymer composites, adsorbents or salts but another interesting strategy is to solve the available Al and use to synthesize useful materials [3,4]. Our research group have published various studies about aluminum salts valorization and it applications to synthesize several materials as pure alumina, salts, hydroxides and hydrotalcites [2,5-7].

The main objective of this study is to improve and determine the conditions for aluminum extraction using NaOH from aluminum saline slags. Previous studies carried out by other authors use a single stage to extract aluminum [8-13], leaving more aluminum in the residue that could be extracted and used. The treatment performed removes the toxic compounds from the saline slag to become a non-hazardous waste that can be handle as by-product [7]. As a second objective, the study included the extraction of aluminum from the waste to synthetize other materials with added value as hydrotalcites, among others [6,14].

2. Experimental

2.1 Materials

The waste employed in this work came from *Iberica de Aleaciones Ligeras S.L. (IDALSA)*, that is a medium Spanish company that has the best available fusion technologies for the recycling of aluminum by-products and their transformation into ingots of various shapes and chemical compositions [15]. The aluminum saline slag that generates in its processes is a very powdered solid and consisted mainly (>50 wt.%) of particles less than 23 mm in diameter. It is the hazardous waste used in this study, named as original waste and denoted as W.

The milling of the aluminum saline slag is made in a bench-top grinding ball mill with alumina balls of 10 mm diameter.

The alkaline extraction was performed in a glass Erlenmeyer of 1 dm^3, with a double cooling condenser 24/40 200 mm. Heat and stirring were applied with a magnetic stirrer with hot plate. The reagent used for the alkaline extraction of the aluminum saline slags was NaOH (Panreac). Filtration of the alkaline treated aluminum saline slag was made with a Büchner funnel connected to a Büchner flask by a rubber bung, with a tube leading to a vacuum pump and using a paper filter of 47 mm, 10-13 μm pore diameter, 0.180 mm thickness, 87 g/m^2 retention.

2.2 Extraction procedure and waste separation

The starting point and reference conditions for this study come from the experience of our research group [7] about alkaline extraction of Al from aluminum saline slags: 37.5 g of hazardous waste is treated under reflux and stirring with 0.75 cm^3 of 2 mol/dm^3 aqueous solution of NaOH for 2 h. So, the ratio waste/NaOH is 1:20 g/dm^3.

The parameters of alkaline extraction that were studied and determined in this research are: particle size of the aluminum saline slag, NaOH concentration,

extraction time, single or multiple consecutive extractions from 1 to 4. Single extraction, denoted as 1 extraction, applies the alkaline treatment to the hazardous original waste (W) one time and generates and an alkaline solution (D1) and a residual waste (RW1). Double extraction, 2 consecutives extractions, applies the alkaline treatment to W and after filtering makes the same alkaline treatment to RW1, generating D2 and RW2. Triple extraction, 3 consecutives extractions, applies the alkaline treatment to W, generating D1 and W1, after filtering makes the same alkaline treatment to RW1, generating D2 and W2, and after filtering makes alkaline extraction with RW2, generating D3 and RW3. Quadruple extraction, 4 consecutives extractions, applies the alkaline treatment to W, generating D1 and W1, after filtering makes the same alkaline treatment to RW1, generating D2 and W2, after filtering an alkaline extraction with RW2, generating D3 and RW3 and after filtering applies the last alkaline extraction to RW3, generating D4 and RW4. This procedure is an Al multistage crosscurrent leaching with NaOH (see Figure 1). Leaching experiments of the deliverable Al in the aluminum saline slags were proposed in a crosscurrent system compound of 4 stages, where the solid phase is the same in all the stages (A) and the solvent flow is renovated in each of them. In each stage the non-soluble solids (B) are mixed with the solute B and the solvent C. The concentration of humid inert are defined as N = B mass / (A+C) mass. The solute concentration in the liquid flows is x_i, x_i = mass C / mass (A+C) and in the solids flows, y_i, y_i = mass C/mass (A+C). Supposing that the extracted Al is not adsorbed on the surface of the inert and that the solution associated to the solid flow and the liquid have the same composition, in a diagram x, y vs. N the equilibrium it is represented by a horizontal line denoted as $N_{Equilibrium}$. The solid phase used in the first stage is denoted as N_{Feed} and NaOH solution is R_0. The humid solid flows generated in each stage are E1, E2, E3 and E4. Solvent flows with leached Al are R1, R2, R3 y R4. And the mix points M1, M2, M3 y M4.

The aluminum saline slag previously treated with hot water was used as the material. The milling of the aluminum saline slag to activate it for the extraction [16] is made in a bench-top grinding ball mill with alumina balls of 10 mm diameter for 3 and 8 h. The chemical composition and structure of this hazardous waste is

characterized and compared with the residual wastes generated in the alkaline extractions.

The samples prepared and studied are summarized in Table 1. The nomenclature used is *Sxyzt*, where *x* is the milling time, *y* is the NaOH concentration, *z* is the extraction time and *t* is the number of extractions.

As the Al extraction has made under reflux, NH_3 and all the other volatile compounds could be removed. However, as the alkaline extraction medium is high concentrated NaOH aqueous solution, what is a toxic compound and very reactive with water, the residual waste generated is contaminated with NaOH. Because of that, it is also a hazardous waste. Once the parameters of extraction have been determined, the purification of the residual waste after filtration is studied in order to transform it to a non-hazardous waste, by cleaning and filtering it with deionized water, and then drying it at 120 ºC for 4 h.

2.3 Characterization techniques

Al and Si extracted in the aqueous solution were determined by inductively coupled plasma optic emission spectroscopy (ICP-OES) with a VARIAN ICP-OES VISTA MPX with radial vision.

The aluminum saline slag (original waste) and the residual wastes generated in the alkaline extractions were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), energy-dispersive X-ray (EDX), scanning electron microscopy (SEM) and N_2 adsorption measurements at -196 ºC.

The powder XRD patterns of the original and residual wastes were made using a SIEMENS D-5000 diffractometer, to determine their composition and structure. The aluminum saline slag was directly analyzed without any previous treatment. The generated wastes were purified with deionized water and dry at 120 ºC for 4 h before the test.

The chemical composition of the wastes was determined with a sequential mass spectrometer of wave dispersion X-ray fluorescence (WADXRF) PANalytical

under vacuum. Before characterization, samples were calcined al 1050 ºC for 1 h and agglutinated with Elvacite. The loss of ignition (LOI) of the samples is calculated heating an aliquot portion of each sample at 1050 ºC for 1 h in a muffle. The values are expressed as weight% of oxides, except Cl and F. In the characterization by energy-dispersive X-ray values are expressed as weight% of elements and atoms.

SEM analysis of the samples was made using a JEOL microscope, model JSM-6400. Images of the samples were taken at 100, 10 and 1 μm scales to determine size and shape of the particles.

N_2 (Praxair, 99.999%) adsorption measurements were obtained at -196 °C from a Micromeritics ASAP 2020 Plus adsorption analyzer. The Brunauer-Emmett-Teller (BET) specific surface area is calculated in the relative pressure range of 0.05-0.20 and the total pore volume at a relative pressure of 0.99.

3. Results and discussion

3.1 Aluminum saline slag characterization

The chemical composition of the major elements that compound the original waste was determined by XRF. The values are expressed as weight % of oxides, except Cl y F that are written as weight % of elements, and presented in Table 2. These results show that the content of the main constituents (i.e. Al and Si) are Al_2O_3 54.41 wt.% and SiO_2 5.69 wt.%, so the SiO_2/Al_2O_3 ratio in the original waste is 0.10.

The chemical composition of aluminum saline slags is very complex and depends on the raw material used [17,18]. The main crystalline phases determined by XRD by various authors include aluminum oxide (various phases), metallic Al, aluminum nitride, magnesium aluminate, magnesium oxide, magnesium silicate and calcium aluminate. No other compounds or elements were detected in any of the samples characterized. They may be in the form of amorphous phases or also as crystalline phases but in very low amounts, in both cases not detectable by XRD [7]. According to the tabulated data, XRD peaks for AlN hexagonal (wurtzita structure) are 33.1° (100), 35.9° (002), 37.8° (101) and 49.8° (102). AlN cubic (zinc-blenda

structure) has a peak in 38.5° (111). XRD peaks for Al metallic are 38º (111), 44º (220) and 65º (220). For Al_2O_3, XRD peaks are 25.51º (012), 35.13º (104), 37.62º (110), 43.23º (113), 52.42º (024), 57.44º (116), 66.30º (214), 67.90º (330), 76.97º (1010) and 89.00º (0210), for spinel 19º (111), 31.5º (220), 37º (311), 45º (400), 56º (422), 60º (511), 65º (440) and 68º (531). As it is shown in Figure 2, XRD pattern of the aluminum saline slag (W) shows 4 crystalline phases: corundum (Al_2O_3), aluminum nitride (AlN), metallic aluminum (Al) and spinel ($MgAl_2O_4$) [7,16]. As the deliverable Al of the aluminum saline slag are the metallic Al and the AlN [12], these materials have been identified and compared in the original and residual wastes. The aluminum saline slag is grey before calcination and brown after it. This change in the color of the original waste is caused by the elimination of the volatile components in the calcination, and also due to the oxidation of some elements or molecules in this process. Any case, XRD analysis shows the same profile for both samples of aluminum saline slag, but it is clear in the calcinated waste, what reveal that calcination is a purification method for the original waste.

The chemical composition of the aluminum saline slag before the Al extraction with NaOH, the original waste, and after it, the residual wastes, are calculated from the results of XRF and XRD. The values, expressed in weight %, are summarized in Table 3 and Figure 3. These results show that the deliverable aluminum, metallic Al and AlN, in the original waste is 19.2 wt.% and it is completely solved with this alkaline extraction procedure and are not present in residual wastes. They also show that Al from corundum and spinel are not solved with NaOH because their values are the same in the residual wastes. The value of corundum increases because some of the Al is oxidized in the extraction and/or the purification. The quantity of non-crystalline components and the LOI is higher in the original wastes than in the original because Al is extracted, and volatile components are removed.

The textural results from N_2 adsorption at -196 °C for the initial waste and the residual wastes generated in the extractions with NaOH are summarized in Table 4. The measurements reveal that the aluminum saline slag (W) has the higher BET surface area and the smaller size and pore volume in comparison to the other solids.

3.2 Al and Si extracted in the aqueous solution

As it has been previously commented, the deliverable Al of the aluminum saline slag are the metallic Al and the AlN. The chemical reactions for Al extraction with NaOH are:

Al extraction from metallic Al

$$Al + NaOH + H_2O \longrightarrow Na(Al(OH)_4) + H_2 \quad (1)$$

Al extraction from AlN

$$AlN + NaOH + H_2O \longrightarrow Na(Al(OH)_4) + H_2 \quad (2)$$

The Al and Si extracted in the aqueous solution are quantitatively determined by ICP-OES. The reference aqueous solution, obtained by a single extraction with NaOH 2 mol/dm^3 for 2 h, has 6.75 g/dm^3 of Al (13.5 %) and 0.30 g/dm^3 of Si (0.6 %), so the ratio Si/Al is 0.04. Comparing the results of single and multiple consecutive extractions in these extraction conditions, it is appreciated that the content in Al in the 2nd consecutive extraction is 5 times lower than in the 1st one and it decreases to zero in the 3rd and 4th consecutive extractions (see Table 5 and Figure 3). The extractions made with NaOH 1 mol/dm^3 confirm that the 1st extraction dissolves high quantity of Al and very low of Si, but the Al extracted with NaOH 1 mol/dm^3 is 80% of the extracted with NaOH 2 mol/dm^3. As the stoichiometry of equations 1 and 2 is 1:1 NaOH:(Al sources), these results indicate that with NaOH 2 mol/dm^3 there are enough NaOH to extract all the deliverable Al in the aluminum saline slag but with 1 mol/dm^3 not. These results also verify that the extraction of Al decreases significantly in the 2nd consecutive extraction and fall to zero in the 3rd and 4th. Regarding the extraction time, Al extractions during 1 h or 4 h are better than in 2 h, and the higher values of Al extracted are obtained in 1 h. The 2nd, 3rd and 4th consecutive extractions do not extract significant Al neither in 1 h nor in 4 h. In relation to milling the aluminum

saline slag before the alkaline extraction, Al extracted is 8% higher when the waste is treated 3 h in the ball mill and 5% higher if the milling is applied for 8 h. These results confirm that milling activates the waste due to the elimination of the surface oxides that protect the waste and limit its reactivity, and also because the total surface area of smaller particles is higher than in bigger ones. According to these results, the best extraction parameters are: activate aluminum saline slag in the ball mill with 10 mm alumina balls for 3 h, and then perform a single extraction to 37.5 g of aluminum saline slag with 0.75 dm^3 of NaOH 2 mol/dm^3 for 1 h, at reflux temperature and with stirring.

This procedure is an aluminum multistage crosscurrent leaching with NaOH and consists in unit operations of solid-liquid extractions in cross currents from 1 to 4 stages. Results show that milling the original waste and perform a single extraction stage maximizes the extraction of the deliverable Al of the aluminum saline slag. The multistage crosscurrent leaching process of the deliverable Al is summarized in Figure 1. The Al concentration in the exit currents of the liquid phases are calculated as g_{Al}/L_{sln}, and the obtained values for R1, R2, R3 and R4 are 15.2, 3.1, 0.5 y 0.1, respectively. These concentrations are similar to the determined in the optimal extraction. Moreover, supposing that the extracted Al is not adsorbed on the surface of the inert and that the solution associated to the solid flow and the liquid have the same composition, in a diagram x, y vs. N the equilibrium it is represented by a horizontal line with a value of 0.2025 kg inert/kg solution, denoted as $N_{Equilibrium}$. Both, the calculated values and the experimental data show that in 1 stage it is extracted the 88% of the deliverable Al, adding a 2nd stage the 96%, with a 3rd stage 99% and in 4 stages the 100%. As adding stages increases the extraction costs, the optimal extraction procedure consists on 2 stages: leaching with NaOH and cleaning with deionized water. This process extracts the 96% of the deliverable Al of the aluminum saline slag and the residual waste is cleaned of the hazardous components of the original waste and the NaOH of the extraction medium. So, residual waste is non-hazardous and has no risk to the environment or the human health.

3.3 Residual waste

As it can be appreciated in Table 2, the SiO_2 wt.% in all the residual wastes is similar as in the original one, what indicates that Si is not extracted. However, the Al_2O_3 wt.% in the residual wastes generated in the Al alkaline extractions are lower than in the aluminum saline slag, which shows that Al is dissolved. The quantity of Al_2O_3 in the 4^{th} extraction of the reference procedure is slightly smaller than in the 1^{st} one which indicates that not much Al is extracted in the 2^{nd}, 3^{rd} and 4^{th} consecutives extractions confirming the results of the alkaline aqueous solutions previously commented. The lower amount of Al_2O_3 is observed in the determined sample what indicates that is the extraction procedure that more Al dissolves and also confirm the results obtained in the characterization of the solutions. These results show that not only the original waste but also the residual wastes generated are valuable sources of Al for other material synthesis. Neither N or other toxic elements are determined, so NH_3 and any other toxic elements are removed. However, XRF results show that the amount of Na in the residual wastes is high and increases progressively in the consecutive alkaline extractions with NaOH what reinforces the idea that a single extraction is better than multiple consecutive extractions. However, the quantity of Na in the determined purified waste is very low, in the same order as in the original waste. This result demonstrates that cleaning the residual waste with deionized water dissolves the NaOH and purified the sample to become a non-hazardous waste.

Residual wastes chemical composition was qualitatively determined by EDX analysis, detecting different metals and metal oxides. Results are summarized in Table 6 and expressed as weight % of the element, not of oxides. These results confirm that the quantities of Al and Si decrease with the extractions and the amount of Na increases, making them hazardous wastes. Moreover, the results show lower composition in Si than in Al, with a Si/Al ratio about 0.10. Neither N or other toxic elements are determined in important quantities, so all toxic elements apart from Na have been removed

As it is shown in Figure 2, the powder XRD pattern for the residual wastes generated after single or multiple extractions with NaOH are very similar to that of the aluminum saline slag (W). These results were expected because the raw sample was previously treated with and alkaline solution at high temperature to remove the soluble salts. The XRD patterns of all the residual wastes present the same peaks as the original hazardous waste in position but with different intensities. The peaks of the single determined extraction peaks present double intensities as their homologous in the original waste XRD pattern. The purification of the hazardous waste due to both the evaporation of the volatile compounds during the extraction at reflux temperature and the cleaning of NaOH and other water-soluble compounds explain this increase in the intensities. XRD analysis have also been performed with the residual wastes raw non-purified and purified, in both cases raw and calcinated. As it is observed in Figure 4, RW is grey before calcination and brown after it. Moreover, after calcination RW1 non-purified and RW1 purified are similar in appearance and the XRD patter also are the same. The XRD patterns of the purified residual wastes only show 2 crystalline phases: corundum (Al_2O_3) and spinel ($MgAl_2O_4$). Aluminum nitride (AlN) and metallic aluminum (Al) are not detected, what confirm that this Al has been extracted with NaOH. There are not peaks from NaOH, Na_2CO_3 or Na_2O, confirming that the purification procedure used removes them. Although W4 is purified by the same procedure as W1, the intensities of the peaks of 4th reference extraction are similar or even slightly smaller than the original waste.

The textural results from N_2 adsorption at -196 °C for the initial waste and the residual wastes generated in the extractions with NaOH are summarized in Table 4. The measurements reveal that the aluminum saline slag (W) has the higher BET surface area and the smaller size and pore volume in comparison to the other solids. These results confirm previous studies of Gil et al [5,7] that states that treatment under reflux conditions with water did not have a marked effect on the textural properties of the initial waste but the specific surface area and pore volume change when treated bases. The BET surface area decreases between 40 and 45% in the single extractions with NaOH 2 or 1 mol/dm^3 and also in the determined extraction and falls to 10% in the 4th consecutive extraction. The total pore volume decreases

between 4 and 62%. Average pore sizes increase with treatment, from 14.2 to 24.6 nm.

The morphology changes caused in the original wastes by the consecutive multiple extractions are studied from SEM images of the waste generated after single extraction and after the 4^{th} consecutive multiple extractions (see Figure 5). The particles from W1 show higher size and had the tendency to form aggregates. This characteristic was not showed for the W4.

4. Summary and concussions

Due to its composition and possible reaction with water, the aluminum dross generated in the industrial production of aluminum is classified as a hazardous waste and must be deposited in secure deposits, what not only generates environmental effects but also suppose expensive costs to the industries. In order to valorize it, aluminum saline slags are treated under reflux and stirring with NaOH aqueous solutions and the parameters of alkaline extraction are studied and determined. This procedure consists in unit operations of solid-liquid extractions in cross currents from 1 to 4 stages leaching with NaOH, and results show that milling the original waste, perform a single extraction stage and cleaning with deionized water maximizes the extraction of the deliverable Al of the aluminum saline slag. The best conditions determined are: milling the original waste in a ball mill for 3 h with alumina 10 mm balls and a single extraction with NaOH 2 mol/dm^3 for 1 h.

This study confirms that alkaline treatment of aluminum saline slags with NaOH extracts high quantity of Al and this aqueous solution obtained is a high-added-value product as source of Al. Moreover, as the Al extraction is made under reflux, results reveal that NH_3 and all the other volatile compounds are removed because they are not present in the residual waste generated. However, it is contaminated with Na so is continue being a hazardous waste. Purification of the residual waste by cleaning it with deionized water, filtering and dry at 120 ºC for 4 h transform it to a non-hazardous waste.

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Captions

Table 1. Prepared samples. Nomenclature *Sxyzt*, where *x* is the time of milling, *y* is the concentration of NaOH, *z* is the time of extraction and *t* is the number of extractions.

Table 2. XRF analysis for the samples. Values expressed in wt.% of oxides, except F and Cl.

Table 3. Chemical composition of the aluminum saline slags before the Al extraction with NaOH, the original waste (W), and after it, the residual wastes (RW). Values are expressed in wt.%.

Table 4. Specific surface areas, pore volumes and pore diameters.

Table 5. ICP results for Al extracted aqueous solutions.

Table 6. EDX analysis for the samples. Values expressed in wt.% of oxides, except Cl.

Figure 1. Aluminum multistage crosscurrent leaching with NaOH.

Figure 2. XRD patterns for the samples.

Figure 3. Chemical composition of the waste before and after Al extraction with NaOH.

Figure 4. Original and optimal residual waster, before and after calcination.

Figure 5. SEM images of S0221 (left) and S0224 (right) samples at 100,10 and 1 μm scales.

Table 1. Prepared samples. Nomenclature *Sxyzt*, where *x* is the time of milling, *y* is the concentration of NaOH, *z* is the time of extraction and *t* is the number of extractions.

Sample	Milling (h)	[NaOH] (mol/dm^3)	Extraction (h)	Number of extractions
Reference	**0**	**2**	**2**	**1**
S0221	0	2	2	1
S0222	0	2	2	2
S0223	0	2	2	3
S0224	0	2	2	4
S022t	0	2	2	t=1+2+3+4
S0121	0	1	2	1
S0122	0	1	2	2
S0123	0	1	2	3
S0124	0	1	2	4
S012t	0	2	2	t=1+2+3+4
S3221	3	2	2	1
S3222	3	2	2	2
S3223	3	2	2	3
S3224	3	2	2	4
S8221	8	2	2	1
S8222	8	2	2	2
S8223	8	2	2	3
S8224	8	2	2	4
S0211	0	2	1	1
S0212	0	2	1	2
S0213	0	2	1	3
S0214	0	2	1	4
S0241	0	2	4	1
S0242	0	2	4	2
S0243	0	2	4	3
S0244	0	2	4	4
Optimized	**3**	**2**	**1**	**1**

Table 2. XRF analysis for the samples. Values expressed in wt.% of oxides, except F and Cl that are expressed in wt.% elements.

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O
Original waste	5.69	54.41	1.18	0.21	6.20	2.07	0.89
S0221	5.00	44.46	1.20	0.28	8.82	2.28	11.54
S0224	6.17	43.57	1.49	0.30	9.22	2.96	17.32
Selected purified	4.89	40.39	1.17	0.20	6.05	2.00	1.38
Sample	**K_2O**	**TiO_2**	**P_2O_5**	**F**	**Cl**	**LOI**	
Original waste	0.56	0.56	0.07	0.64	0.58	25.23	
S0221	0.21	0.68	0.07	0.54	0.58	23.43	
S0224	0.20	0.78	0.06	0.48	0.17	16.51	
Selected purified	0.17	0.56	0.10	0.45	0.39	21.21	

Table 3. Chemical composition of the aluminum saline slags before the Al extraction with NaOH, the original waste (W), and after it, the residual wastes (RW).

Compound	**Chemical formula**	**W Waste before Al extraction (wt.%)**	**RW Waste after Al extractions (wt.%)**
Deliverable aluminum: metallic aluminum and aluminum nitride	Al + AlN	19.2	0
Corundum	Al_2O_3	21.7	25.1
Spinel	$MgAl_2O_4$	21.9	21.4
Calcium carbonate	$CaCO_3$	3.7	3.6
Silica	SiO_2	5.7	4.9
Magnetite	Fe_2O_3	1.2	1.2
Sylvite	KCl	0.9	0.3
Titania	TiO_2	0.6	0.6
Total crystalline structures	-	74.8	56.9
Non-crystalline and LOI	-	25.2	43.1

Table 4. Specific surface areas, pore volumes and pore diameters.

Sample	S_{BET} (m^2/g)	V_{pT} (cm^3/g)	d_{pBJH} (nm)
W	129	0.197	6.1
S0221	56	0.249	17.8
S0221 purified	59	0.298	20.2
S0121	54	0.251	18.4
S3211	48	0.170	14.2
S3211 purified	66	0.249	15.0
S0224	14	0.067	20.0

Table 5. ICP results for Al extracted aqueous solutions.

Sample	Al (g/dm^3)	Si (g/dm^3)	Al (wt.%)	Si (wt.%)
Reference	**6.75±0.11**	**0.30±0.01**	**13.5**	**0.6**
S0221	6.49±0.19	0.34±0.01	13.0	0.7
S0222	1.22±0.05	0.26±0.01	2.4	0.5
S0223	0.27±0.03	0.22±0.01	0.5	0.4
S0224	0.24±0.03	0.43±0.01	0.5	0.9
S022t	2.20±0.07	0.32±0.01	16.4	2.5
S0121	5.47±0.08	0.20±0.01	10.9	0.4
S0122	1.50±0.05	0.14±0.01	3.0	0.3
S0123	0.43±0.04	0.11±0.01	0.9	0.2
S0124	0.21±0.04	0.13±0.01	0.4	0.3
S012t	1,97±0.07	0.16±0.01	15.2	1.2
S3221	7.03±0.15	0.27±0.01	14.1	0.5
S3222	1.75±0.03	0.23±0.01	3.5	0.5
S3223	0.24±0.02	0.27±0.01	0.5	0.6
S3224	0.57±0.02	0.27±0.01	1.1	0.5
S8221	6.79±0.16	0.31±0.01	13.6	0.6
S8222	1.69±0.15	0.25±0.01	3.4	0.5
S8223	0.38±0.06	0.29±0.01	0.8	0.6
S8224	0.15±0.06	0.23±0.01	0.3	0.5
S0211	7.54±0.18	0.37±0.01	15.1	0.7
S0212	1.00±0.09	0.22±0.01	2.0	0.4
S0213	0.17±0.06	0.16±0.01	0.3	0.3
S0214	0.08±0.07	0.13±0.01	0.2	0.3
S0241	7.02±0.73	0.18±0.01	14.0	0.4
S0242	1.70±0.15	0.27±0.01	3.4	0.5
S0243	0.48±0.06	0.41±0.01	1.0	0.8
S0244	0.17±0.06	0.33±0.01	0.3	0.7
Selected	**7.72±0.10**	**0.32±0.01**	**15.4**	**0.6**

Table 6. EDX analysis for the samples. Values in wt.%.

Sample	O	Na	Mg	Al	Si	P	S	Cl
S0221	43.00	7.00	6.70	27.00	2.60	0.14	0.07	0.41
S0224	39.00	29.00	1.90	9.00	2.00	0.13	0.06	0.03
Sample	**K**	**Ca**	**Ti**	**Cr**	**Mn**	**Fe**	**Cu**	**Total**
S0221	0.18	1.70	0.50	0.11	0.30	1.40	0.90	92.00
S0224	0.16	0.93	0.28	0.10	0.30	0.70	0.51	84.00

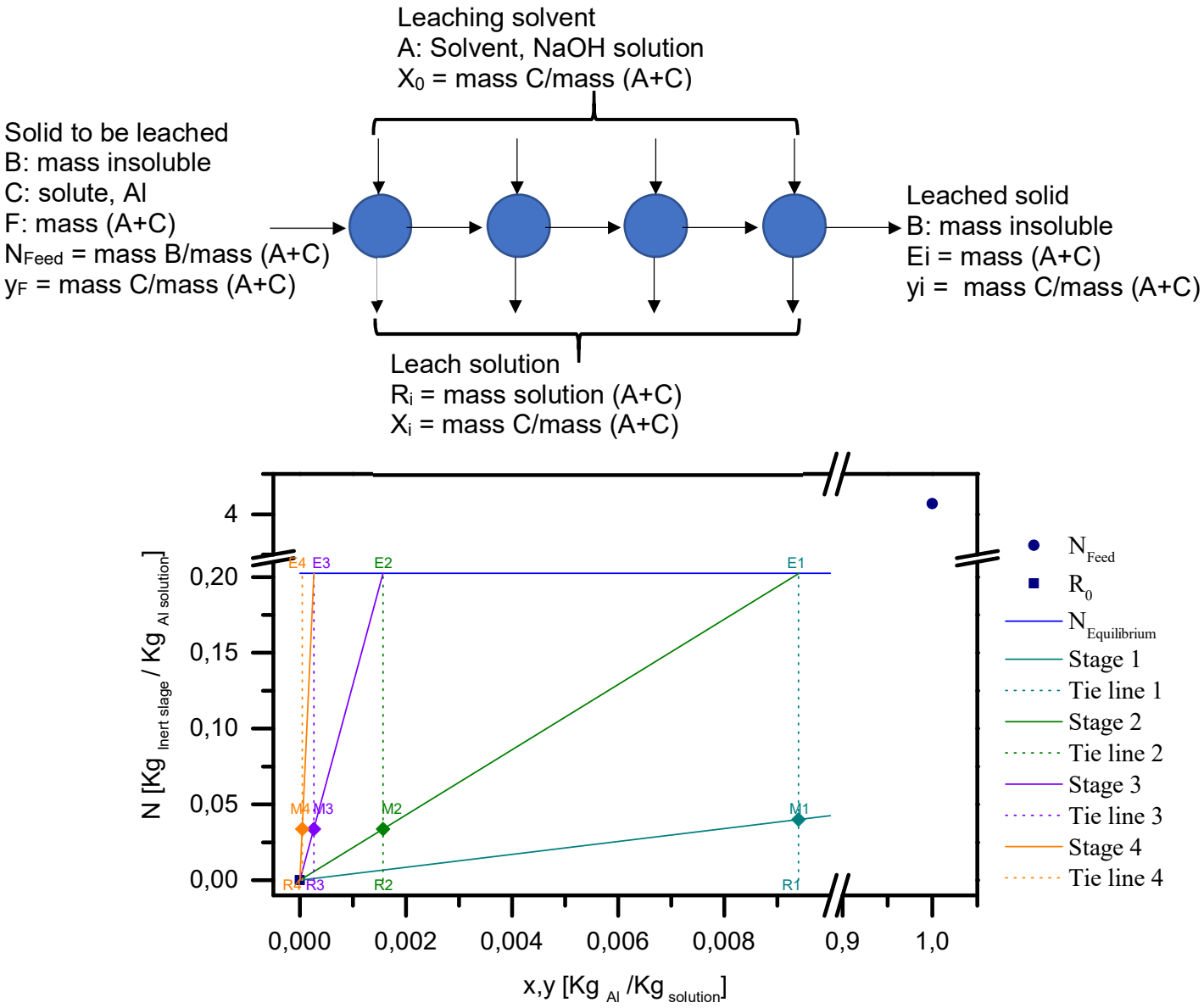

Figure 1. Aluminum multistage crosscurrent leaching with NaOH.

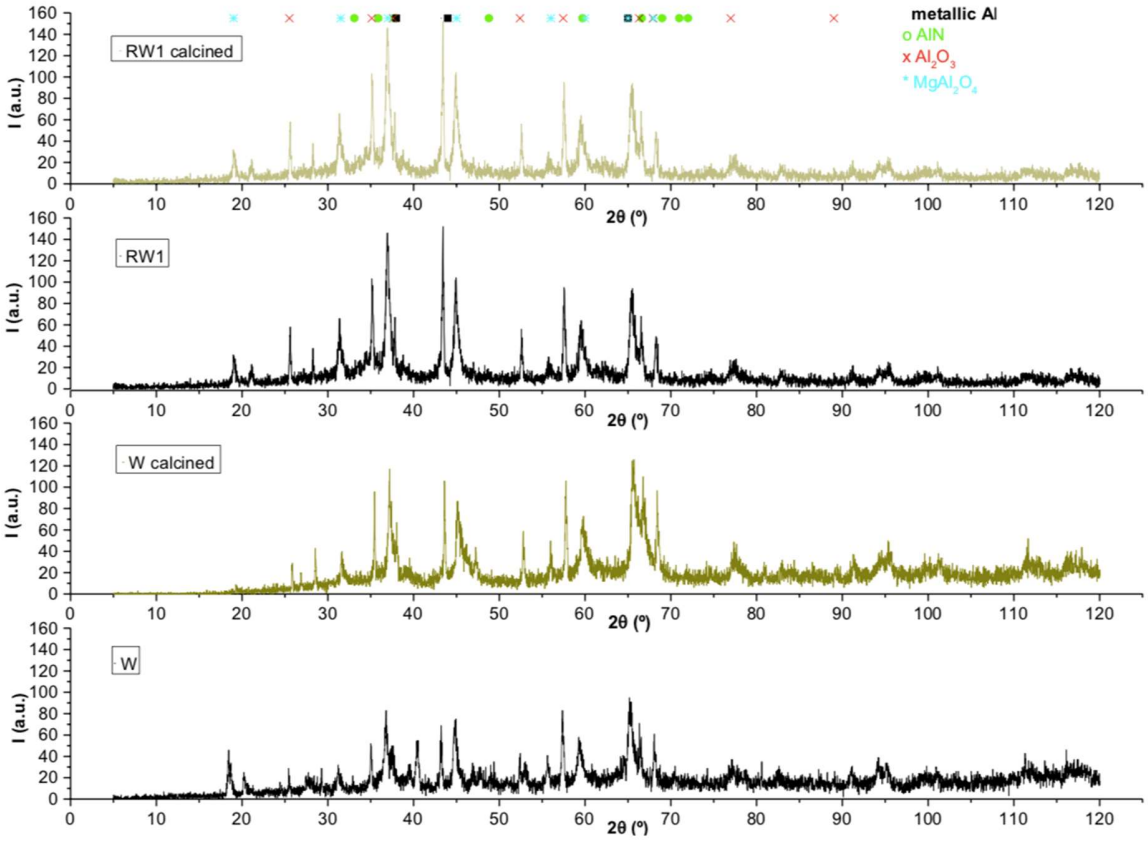

Figure 2. XRD patterns for the samples.

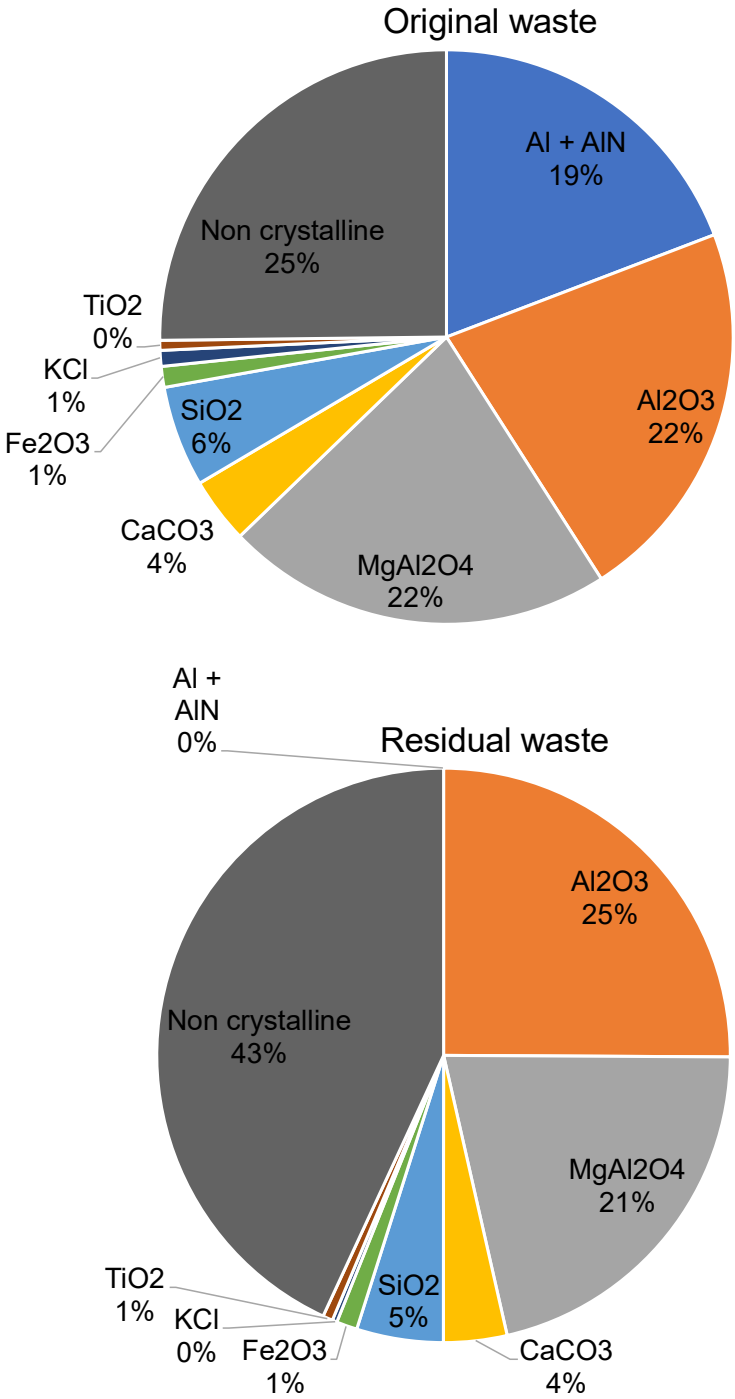

Figure 3. Chemical composition of the waste before and after Al extraction with NaOH.

Figure 4. Original and final residual waste, before and after calcination.

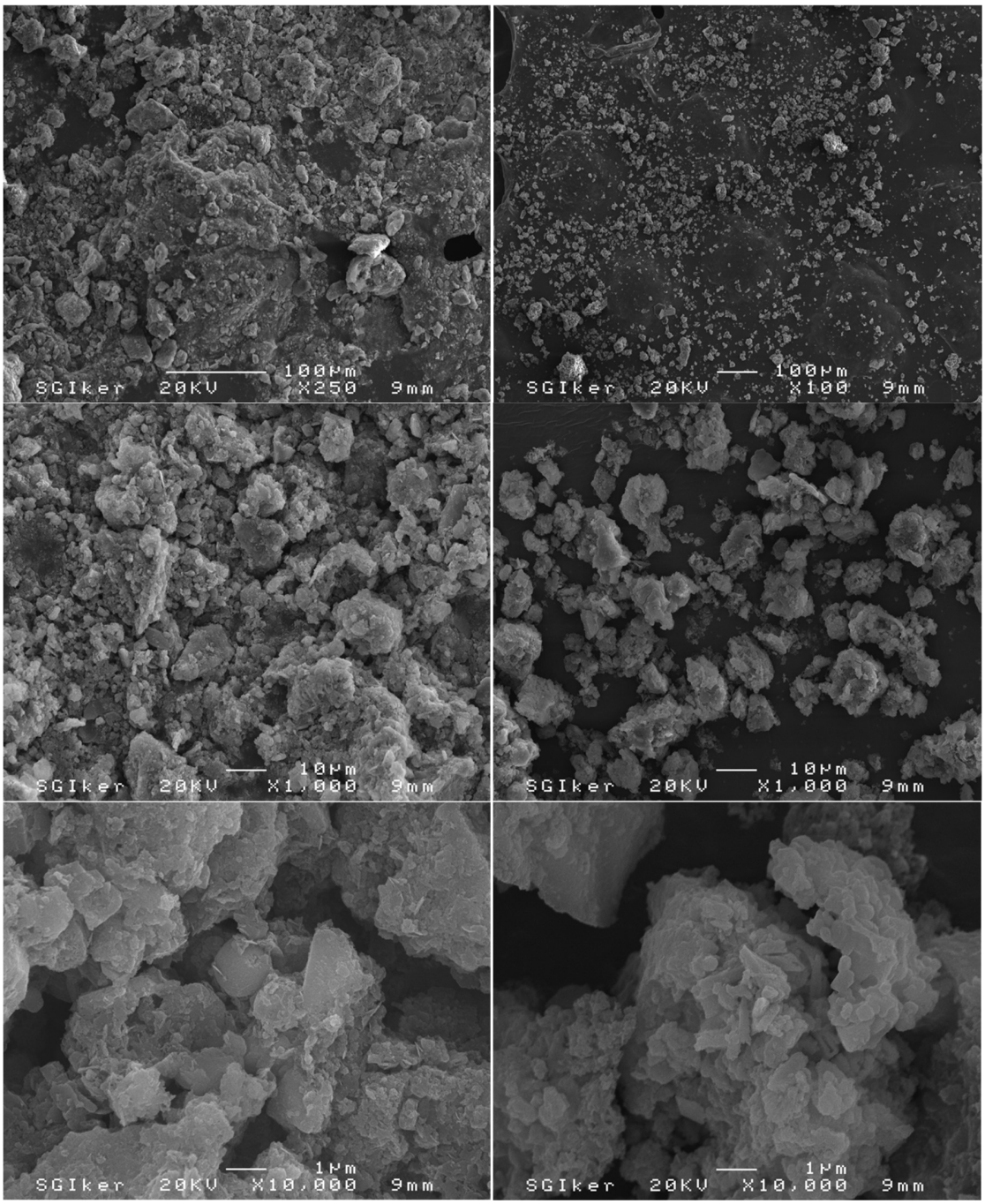

Figure 5. SEM images of S0221 (left) and S0224 (right) samples at 100,10 and 1 μm scales.